

A Matrix Isolation and Computational Study of Molecular Palladium Fluorides: Does PdF₆ Exist?

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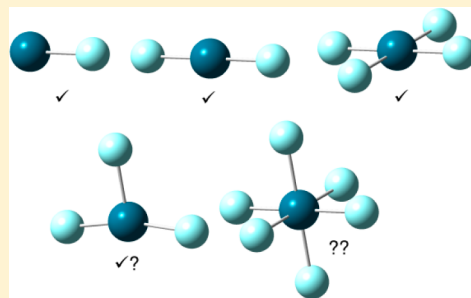
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Supporting Information

ABSTRACT: Palladium atoms generated by thermal evaporation and laser ablation were reacted with and trapped in F₂/Ar, F₂/Ne, and neat F₂ matrices. The products were characterized by electronic absorption and infrared spectroscopy, together with relativistic density functional theory calculations as well as coupled cluster calculations. Vibrational modes at 540 and 617 cm^{−1} in argon matrices were assigned to molecular PdF and PdF₂, and a band at 692 cm^{−1} was assigned to molecular PdF₄. A band at 624 cm^{−1} can be assigned to either PdF₃ or PdF₆, with the former preferred from experimental considerations. Although calculations might support the latter assignment, our conclusion is that in these detailed experiments there is no convincing evidence for PdF₆.



INTRODUCTION

There has been considerable recent activity in understanding the limits of stability of the high oxidation states of 4d and 5d transition metal complexes.^{1,2} In this context, the question of whether mercury should be regarded as a transition metal has been raised.^{3–6} There is compelling experimental evidence for the 4d hexafluorides of Mo to Rh and the 5d hexafluorides of W to Pt,^{7,8} as well as ReF₇.⁹ Computational investigations (density functional theory (DFT) and state-of-the-art coupled-cluster (CC)) have indicated the stability of Pd(VI) in PdF₆ (DFT,^{10–13} CC¹²); Tc(VII) in TcF₇ (CC);¹⁴ Ir(VII) in IrF₇ (CC);¹⁵ and that Os(VII) and Os(VIII) might exist as OsF₇ and OsF₈ (CC).¹⁶ However, calculations indicate that AuF₆ and AuF₇ are unlikely to be stable¹⁷ (despite the reported preparation of AuF₇^{18,19}) and that platinum fluorides higher than PtF₆ are also unlikely to be stable.^{20,21} In addition, calculations indicate the stability of Rh(VIII) in RhO₄,²² Ir(VIII) in IrO₄,²³ and even Ir(IX) in [IrO₄]⁺.^{24–26} There is a lone experimental report of the preparation of PdF₆, but its identification rests on a single IR band at 711 cm^{−1},^{27,28} and this has been questioned on the basis of calculations.^{1,10} It is reported that the only “real” Os(VII) compound known experimentally is OsOF₅ and that when the published conditions for the synthesis of OsF₇ were repeated, only OsF₆ was obtained.²⁹ Although there is reported evidence for IrO₄ with Ir(VIII) in low-temperature matrices,²³ there was no evidence for Rh(VIII) in analogous experiments.²² In addition

to being vital to understanding the limits of chemical stability, the more stable, high oxidation state fluorides can be used as potent oxidizers.^{30,31}

Of the “missing” hexafluorides,² PdF₆ is probably the most surprising, given that all the other 4d and 5d hexafluorides of groups 6–8 are known,^{7,8} including PtF₆,^{32,33} which was instrumental in the development of xenon chemistry as long ago as 1962.^{34,35} There appear to be no experimental reports on PdF. PdF₂ adopts the rutile structure in the solid state.³⁶ PdF₃ is mixed valence, containing Pd(II)[(Pd(IV)F₆)]₂, with both palladium atoms in an octahedral environment.^{37–40} PdF₄ is diamagnetic and has octahedral coordination in the solid state with two terminal cis F atoms and four bridging F atoms.^{41,42} Note that, while XeF₂ will oxidize PtF₄ and “PdF₃”, it will not oxidize PdF₄.³⁹ Apart from the single report on PdF₆,^{27,28} there appears to be no other experimental data available for the molecular palladium fluorides, including PdF. However, there has been considerable computational activity in recent years because of the possibility of both Jahn–Teller and spin–orbit effects manifesting themselves.^{10–13,43–47}

Here we report an experimental and quantum-chemical investigation of the binary palladium fluorides from PdF to PdF₆. Several matrix-isolation setups around the world (U.K., U.S., and Germany) were involved in these experiments using

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both thermal evaporation and laser ablation to generate palladium atoms for reaction with F₂-doped Ar and Ne matrices as well as neat F₂ matrices. In addition quantum-chemical calculations utilizing both relativistic DFT and CC were performed to characterize the species in question.

EXPERIMENTAL AND COMPUTATIONAL DETAILS

The matrix isolation equipment used for thermal evaporation^{48–50} and laser-ablation experiments^{51–53} has been described in detail before. The thermal evaporation studies performed at the University of Hull used palladium wire (0.1 mm, 99.99% Goodfellow) wound around and within three strands of a tantalum wire hairpin former (0.5 mm, 99.99% Goodfellow), which was heated using ca. 40 A at 1 V. To avoid heating of the window and matrix deposit a copper disc with a 5 mm aperture was placed between the furnace and the vacuum chamber containing the deposition window. The F₂/Ar mixtures were prepared using standard manometric procedures from 10% F₂/Ar (Air Liquide) using an all metal vacuum line. The vacuum line, reservoirs, and vacuum chamber were well-passivated. The IR spectra were recorded using KBr beamsplitters and DTGS detectors on Bruker IFS66 and EquNox55 FTIR instruments equipped with APD DE-204 cryostats with base temperatures of ca. 10 K. The electronic absorption spectra were recorded on a Varian Cary SE UV–vis–NIR spectrometer equipped with an APD DE-202 cryostat with a base temperature of ca. 12 K. Broadband photolysis ($\lambda > 250$ nm) was performed with a LOT-Oriel 200 W Hg(Xe) lamp. The laser-ablation investigations performed at the Universities of Freiburg/Berlin and Virginia employed Sumitomo 205 cryocoolers reaching 5 K second stage temperatures and Nicolet 750 (Virginia) or Bruker Vertex 70 (Freiburg/Berlin) FTIR spectrometers equipped with HgCdTe range B liquid nitrogen cooled detectors. The apparatus at Freiburg/Berlin is similar to that at Virginia, but there are differences in Freiburg/Berlin such as the magnetic rotating device for a fixed target, 25 mm of CsI window exposed to the laser-ablation plume, and the lack of a radiation shield. The Virginia experiments with only 12.5 mm of cold window exposed from the OFHC copper mount and radiation shield, employed slightly higher ablation laser energies.

Caution! Fluorine is a powerful oxidizer and toxic. Suitable storage and handling facilities must be used, as well as shielding, protective clothing, and face masks. Extensive care must be taken to avoid contact between fluorine, fluorides, and oxidizable materials. An initial layer of argon should be used to protect the CsI deposition window when neat F₂ matrices are employed.

The simple valence force field calculations (SVFF) utilized SOTONVIB.⁵⁴ DFT calculations were performed using the ADF program^{55–57} at the BP86^{58–60} level with triple- ζ (TZ2P) Slater-type orbital basis sets and relativistic effects at the ZORA level.⁶¹ Spin-orbit coupling was included, as appropriate, in the structure optimizations and in analysis of the thermochemistry. Zero point and basis set supposition error corrections were also incorporated in the thermochemical analysis. Harmonic frequency calculations were performed at all optimized structures. Beyond the investigations using the ADF code we also performed DFT calculations using Gaussian09,⁶² and for CC, the CFOUR program package was used.⁶³ Structure optimizations for all possible spin states were first performed using the B3LYP functional with the aug-cc-pVTZ basis set for fluorine and the aug-cc-pVTZ-PP basis set for Pd using the relativistic small core pseudopotential of the Stuttgart–Koeln type (MCDHF RSC ECP).⁶⁴ The most stable configuration was then used as the starting structure for the CC calculations. Harmonic frequency calculations were performed at all optimized structures.

RESULTS

The key to interpreting the matrix IR data is (i) identifying the vibrational modes that involve Pd and F, (ii) determining the number of fluorine atoms coordinated to the Pd, and (iii) confirming the molecular shape of the PdF_n species formed. Unfortunately, F is monoisotopic so determining the PdF coordination number is not straightforward from the vibrational

data alone. However, Pd does have isotopes that are sufficiently well-separated to give observable isotope patterns in well-resolved matrix IR data. Figure 1 displays a series of SVFF

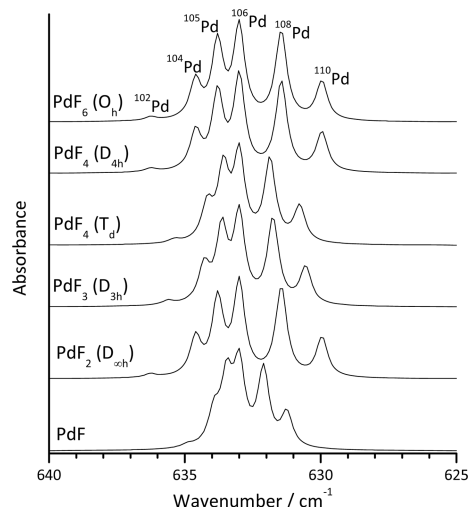


Figure 1. SVFF calculated palladium isotope patterns for IR active modes in a variety of prototypical geometries.

calculated Pd isotope patterns for the IR-active $\nu_{\text{Pd-F}}$ modes of different PdF_n species using the same transition wavenumber (¹⁰⁶Pd at 633.0 cm^{−1}) and bandwidth (0.5 cm^{−1} fwhm). While it is clear that the pattern expected for PdF (and “PdF” units) is reasonably distinct from the others with a separation of ca. 0.9 cm^{−1} between the ¹⁰⁶PdF and ¹⁰⁸PdF components, the calculated patterns for the other stoichiometries and geometries are more similar. The ¹⁰⁶PdF and ¹⁰⁸PdF separation is 1.5 cm^{−1} for linear PdF₂, 1.25 cm^{−1} for 120° in PdF₃, and 1.15 cm^{−1} for 109.47° in tetrahedral PdF₄. The calculated IR Pd isotope patterns for D_{4h} PdF₄ and O_h PdF₆ are essentially identical to that of linear PdF₂ as the E_u (D_{4h}) and T_{1u} (O_h) modes are essentially just orthogonal PdF₂ asymmetric stretching modes. Likewise, the pattern for D_{3h} PdF₃ is essentially identical to that from PdF₂ with a 120° bond angle, and that from T_d PdF₄ is the same as that for a PdF₂ unit with a 109.47° bond angle. Therefore, these calculations show that PdF will give rise to a characteristic isotope pattern but that the spectra of linear PdF₂, square planar PdF₄, and octahedral PdF₆ will be essentially identical in terms of both the number of bands expected and the Pd isotope structure on them. Any deviation from linearity of the “PdF₂” units will result in a reduced separation of the Pd isotopic features, but for slight distortions from linearity this will be fairly small due to the nature of the sine function. Therefore, while it will be possible to identify PdF modes belonging to PdF_n species from the characteristic palladium isotopic structure, it is anticipated that assignment of the IR features to individual compounds will be challenging and that insights from computational chemistry will be vital to obtaining a full assignment.

Computational Chemistry. Care needs to be exercised to get an accurate description of the palladium fluorides because of the possibility of considerable Jahn–Teller, spin–orbit, and relativistic effects. While there have been a number of computational reports on the palladium fluorides,^{10–13,43–46,65–68} there is no systematic study of all possible PdF_n species available in the literature. As it is anticipated that there will be a mixture of species formed, a

detailed computational study of the ground-state structures, spin states, and vibrational data as well as selected thermochemical values was performed for PdF_n ($n = 1$ to 6) using both DFT and CCSD methods. As it has been shown previously that spin–orbit coupling needs to be included,^{11,69} we concentrated on the results of our relativistic DFT calculations, which include spin–orbit coupling, and the calculated ground-state structures, electronic ground terms, and vibrational data for PdF_n ($n = 1$ –6) are given in Table 1.

Table 1. Summary of Relativistic DFT Computational Results^a

			Pd–F (Å)	F–Pd–F (deg)	$\nu_{\text{Pd–F}}$ modes/ cm^{-1} (symmetry species, IR intensity)
PdF	$C_{\infty v}$	$^2\Sigma^+$	1.930		533.9 (Σ^+ , 41)
PdF ₂	$D_{\infty h}$	$^3\Pi_g$	1.895	180	633.5 (Σ_g^+ , 146), 560.9 (Σ_g^+ , 0)
PdF ₃	C_{2v}	2A_2	1.865 (x2)	168.0	661.8 (B_2 , 117), 591.9 (A_1 , 0.86), 565.3 (A_1 , 39.7)
			1.886	96.0	
PdF ₄	D_{4h}	A_1 (3E_g)	1.866	90	663.5 (E_g , 81.6×2), 585.6 (A_{1g} , 0), 523.7 (B_{1g} , 0)
PdF ₅	C_{4v}	2B_2	1.878 (x4)	173.03	648.3 (E , 79.1×2), 632.7 (A_1 , 15.5)
			1.854	93.5	578.6 (A_1 , 0.95), 552.6 (B_1 , 0)
				89.8	
PdF ₆	O_h	A_1 ($^3T_{1g}$)	1.876	180, 90	648.0 (T_{1u} , 58.7×3), 574.0 (A_{1g} , 0), 541.2 (E_g , 0 x2)

^aADF, BP86, TZ2P, ZORA.

For PdF_4 and PdF_6 there is considerable debate about whether the structures are Jahn–Teller distorted or subject to spin–orbit effects that quench this distortion and whether the deviations from regular D_{4h} and O_h geometries would be detectable.^{10–12,46,69} Our calculations using DFT and CCSD without spin–orbit coupling, together with a summary of earlier data,^{10,11,13,43,44} are given in the Supporting Information. (There is one computational report that deals with many PdF_n species.¹³ However, no ground terms or vibrational energies are given, many of the geometries are different to previous calculations, and the electronic configuration of Pd is reported as $[\text{Kr}]4d^{10}5s^1$; therefore, we have not included these results in our discussion.)

PdF is predicted to have a $^2\Sigma^+$ ground state, in agreement with Schwerdtfeger,⁶⁵ Siegbahn,⁴³ and Cheng.⁴⁵ Our calculated Pd–F distance is 1.930 Å compared to 2.01 Å from Siegbahn⁴³ and 1.961 Å from Cheng.⁴⁵ The harmonic frequency of 533.9 cm^{-1} is very similar to that of 531 cm^{-1} calculated by Cheng.⁴⁵

PdF_2 is calculated to have a linear, $^3\Pi_g$ ground state, based on a $(\delta_g)^4(\pi_g)^3(\sigma_g)^1$ ligand-field occupation, with the IR-active Σ_g^+ ν_{PdF} mode at 633.5 cm^{-1} . The $^3\Sigma_g^+$ state was calculated to lie ca. 20 kJ mol^{-1} higher than the $^3\Pi_g$ ground state. The lowest-energy singlet is found to be strongly bent, with a bond angle of 102°, and ca. 40 kJ mol^{-1} higher than the $^3\Pi_g$ ground state. The lowest-energy linear singlet state is ca. 50 kJ mol^{-1} higher in energy. Siegbahn also predicted a $^3\Pi_g$ ground state for PdF_2 .⁴⁴ The PdF_2 bond length is calculated to be 1.895 Å, compared to 1.94 Å from Siegbahn.⁴⁴ In contrast, Wesendrup and Schwerdtfeger²⁰ found a linear, triplet $^3\Sigma_g^+$ ground state for PtF_2 , based on the ligand-field occupation $(\delta_g)^4(\sigma_g)^2(\pi_g)^2$.

PdF_3 is calculated to have a spin-doublet (2A_2) T-shaped structure with one longer (1.886 Å) and two slightly shorter (1.865 Å) Pd–F bonds. The IR-active ν_{PdF} modes are predicted to be at 661.8 cm^{-1} (B_2), 591.9 cm^{-1} (A_1), and 565.3 cm^{-1} (A_1) with an intensity ratio of 136:1:46. A recent theoretical report on XePdF_3 has indicated a T-shaped structure with C_1 point group for PdF_3 , but no bond lengths or angles were given.⁶⁸ This work also highlighted the challenge these types of molecules present to computational chemistry.

Optimization of the ground state of PdF_4 leads to a very slightly distorted square planar molecule based on a Jahn–Teller distortion of the 3E_g state. The D_{2d} geometry is very slightly nonplanar with bond angles that alternate by less than 0.5° in keeping with the results obtained by Aullón and Alvarez for PdF_4 ¹⁰ and for PtF_4 by Wesendrup and Schwerdtfeger.²⁰ However, when spin–orbit coupling is included, even this small distortion is quenched, yielding a D_{4h} structure with an A_1 ground state, 1.866 Å bond lengths, and a single IR-active ν_{PdF} mode at 663.5 cm^{-1} . Figure 2 shows the effect of spin–orbit

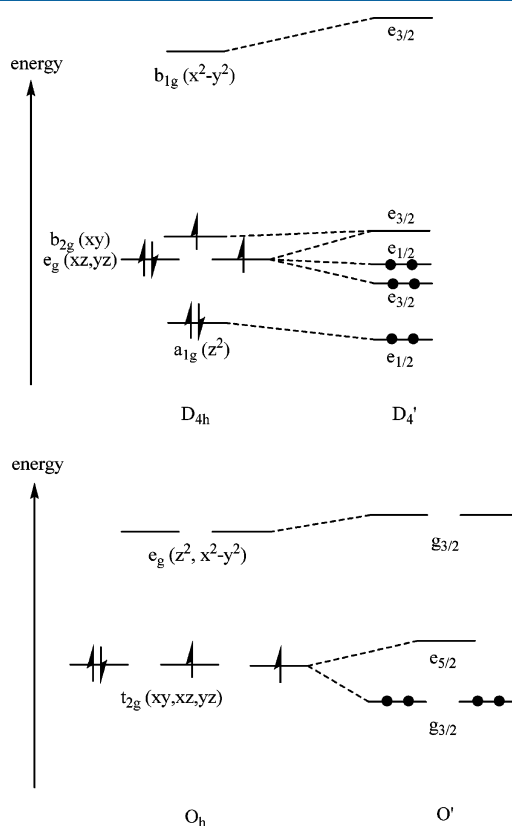


Figure 2. Effect of spin–orbit coupling on the d orbitals of PdF_4 (top) and PdF_6 (bottom).

coupling on the d-orbitals with loss of the orbital degeneracy responsible for the Jahn–Teller activity. This observation is in keeping with that of David et al. for the hexafluorides.^{11,69,70} Our CCSD calculations without spin–orbit coupling retain a planar, distorted D_{2h} structure with 1.805 and 1.848 Å Pd–F distances. These CCSD calculations indicate that there will be two IR-active ν_{PdF} modes, at 750.4 and 707.7 cm^{-1} .

PdF_5 is calculated at the relativistic DFT level to have a square-pyramidal (C_{4v} symmetry) 2B_2 ground state with an almost square base and with the axial Pd–F bond slightly shorter (1.854 Å) than the equatorial Pd–F bonds (1.878 Å),

with one intense IR band at 648.3 cm^{-1} , together with a weak feature at 632.7 cm^{-1} and a very very weak feature at 578.6 cm^{-1} . The CCSD calculations also yielded a C_{4v} structure, with identical axial and equatorial distances (1.836 Å).

PdF_6 behaves in a similar way to PdF_4 . In the absence of spin–orbit coupling, the $^3T_{1g}$ ground state of octahedral PdF_6 , based on the expected low-spin (t_{2g})⁴ ligand-field configuration, undergoes a very small Jahn–Teller distortion to give a D_{4h} minimum, in keeping with the calculations of Aullón and Alvarez¹⁰ for PdF_6 and Wesendrup and Schwerdtfeger²⁰ for PtF_6 . The inclusion of spin–orbit coupling quenches the distortion so that PdF_6 is predicted to be fully octahedral with an A_1 ground state, a Pd–F bond length of 1.876 Å and the IR-active $\nu_{\text{Pd-F}}$ mode at 648.0 cm^{-1} . This result is consistent with the LDA calculations of David et al. on PdF_6 ¹¹ and the group 11 hexafluoride anions.⁶⁹ Alvarez-Thon et al. have commented that prior to 2008 all of the published nonrelativistic and scalar relativistic calculations had predicted that PtF_6 was a paramagnetic distorted octahedral molecule with a triplet ground state and that the four component spin-free method also predicted a distorted octahedral molecule with axial distortion due to a Jahn–Teller distortion.⁷⁰ However, a diamagnetic, octahedral singlet molecule was predicted when a four-component Dirac molecular Hartree–Fock, DFT, and two-component zeroth-order regular approach (ZORA) methodology was employed. They concluded that the calculated octahedral molecular structure, in agreement with the NMR and vibrational spectroscopic data, was stabilized by the effect of spin–orbit coupling.

Figure 2 illustrates how spin–orbit coupling leads to the loss of the orbital degeneracy in this system. Our CCSD calculations (without spin–orbit coupling) result in a D_{4h} structure with Pd–F of 1.827 and 1.841 Å and two IR-active ν_{PdF} modes at 724.5 and 718.0 cm^{-1} . Craciun et al.¹² predicted that at the CCSD(T)/CBS level the ground state of PdF_6 would be D_{4h} with a $^3A_{1g}$ term but that the O_h structure was within 2 kJ mol^{-1} of this ground-state structure. Their BLYP/TZ2P ZORA spin–orbit calculations predicted that the D_{3d} structure was more stable by 0.5 kJ mol^{-1} . A $^1A_{1g}$ state was found to be ca. 50 kJ mol^{-1} higher in energy than these triplet states. An average Pd–F distance of 1.849 Å was obtained from the CCSD(T) calculations for the D_{4h} structure, compared to an average of ca. 1.91 Å from the BLYP ZORA spin–orbit calculations. The IR-active ν_{PdF} modes were calculated at the B3LYP/ATZ-PP level to be 692 and 671 cm^{-1} .¹² They concluded that because the D_{4h} , D_{3d} , and O_h structures were very close in energy, the 4d MF₆ molecules would be highly fluxional and exhibit an average O_h geometry under most experimental conditions. They also noted that unlike the 5d hexafluorides, the inclusion of spin–orbit effects was unimportant to account for the ordering of the electron affinities. Aullón and Alvarez calculated the B3LYP Pd–F_{eq} and Pd–F_{ax} bond lengths to be 1.894 and 1.890 Å , with IR-active Pd–F stretching modes at 585 and 530 cm^{-1} .¹⁰

The relativistic DFT-calculated vibrational data are in Table 1, and Figure 3 displays the calculated IR spectra to aid with the spectral assignments (the isotopic data is omitted for clarity). From these data it is expected that PdF , PdF_2 , PdF_4 , and PdF_6 will all display one IR-active Pd–F stretching mode, and from the previous discussion the last three will have essentially identical Pd isotope patterns. The calculations also indicate that the most intense $\nu_{\text{Pd-F}}$ modes will be in the wavenumber order of $\text{PdF}_4 \approx \text{PdF}_3 > \text{PdF}_6 \approx \text{PdF}_5 > \text{PdF}_2 \gg \text{PdF}$ (Our CC calculations also indicate that the IR-active vibrational mode of

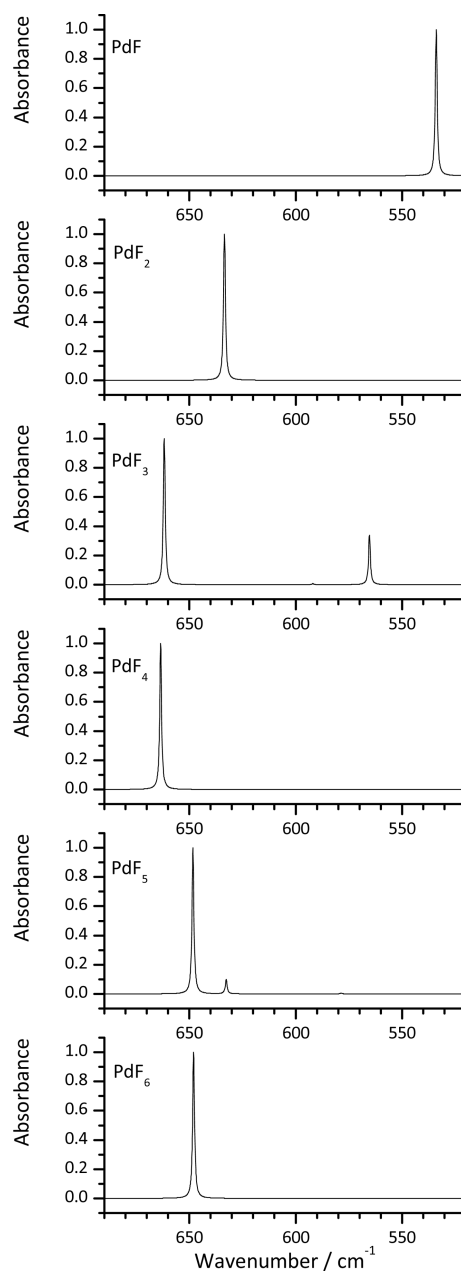


Figure 3. Relativistic DFT-calculated IR spectra for PdF_n species (ignoring Pd isotopes).

PdF_4 will be at higher wavenumber than PdF_6). For PdF_3 two bands are expected, separated by $\sim 100\text{ cm}^{-1}$, with the higher one significantly more intense than the lower one ($\sim 3:1$). The more intense B_2 mode is expected to have a similar isotope pattern to that of PdF_2 , as it is the asymmetric stretch of the bar in the T-shaped molecule. The lower-energy A_1 mode with some IR intensity is predominantly the symmetric stretch of the handle of the T-shaped molecule so will have a Pd isotope pattern more characteristic of a “PdF” unit. Square pyramidal PdF_5 is predicted to have one intense IR-active $\nu_{\text{Pd-F}}$ E mode with a characteristic “PdF₂” isotope pattern, with a weaker A_1 (predominantly axial $\nu_{\text{Pd-F}}$) mode, which may not be detectable above the noise limit. In this case, the separation of the Pd isotope features is slightly larger than that for predicted “PdF₂” and “PdF” units, 1.58 versus 1.50 cm^{-1} and 1.01 versus 0.90

cm^{-1} , but this is very much at the margins of experimental detection.

Therefore, the principal IR-active $\nu_{\text{Pd-F}}$ modes for all of the possible PdF_n species apart from PdF are predicted to have very similar Pd isotope patterns. To complicate matters further, the calculations indicate that the IR-active $\nu_{\text{Pd-F}}$ modes in PdF_3 and PdF_4 will overlap, as will those of PdF_5 and PdF_6 , but that the PdF and PdF_2 $\nu_{\text{Pd-F}}$ modes will be distinct. Aullón and Alvarez calculated that the IR-active $\nu_{\text{Pd-F}}$ modes in PdF_4 and PdF_6 would overlap as well.¹⁰ As noted previously, the published calculated Pd–F stretching modes for PdF_6 range from 585 to 725 cm^{-1} . Hence, an unambiguous assignment will be challenging. However, the fluorine concentration in these experiments will help to identify the higher-valent fluorine species as it is expected that a higher concentration of fluorine will favor the higher-valent palladium fluorides.

The relativistic DFT thermochemical data is collected together in Table 2, and this shows that the formation of all

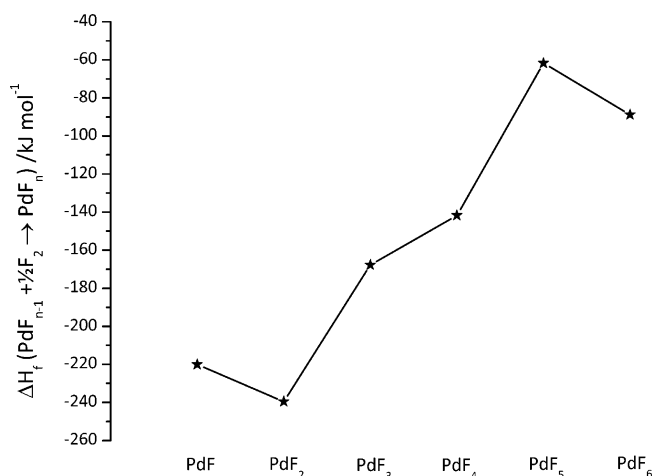


Figure 4. Stepwise formation enthalpies of palladium fluorides.

Table 2. Summary of Thermochemistry from Relativistic DFT Calculations^a

overall ΔH_f	kJ mol^{-1}	stepwise ΔH_f	kJ mol^{-1}	ΔH for selected reactions	kJ mol^{-1}
$\text{Pd} + 1/2\text{F}_2 \rightarrow \text{PdF}$	-220	$\text{Pd} + 1/2\text{F}_2 \rightarrow \text{PdF}$	-220	$2\text{PdF} \rightarrow \text{PdF}_2 + \text{Pd}$	-20
$\text{Pd} + \text{F}_2 \rightarrow \text{PdF}_2$	-460	$\text{PdF} + 1/2\text{F}_2 \rightarrow \text{PdF}_2$	-240	$2\text{PdF}_2 \rightarrow \text{PdF}_4 + \text{Pd}$	150
$\text{Pd} + 3/2\text{F}_2 \rightarrow \text{PdF}_3$	-627	$\text{PdF}_2 + 1/2\text{F}_2 \rightarrow \text{PdF}_3$	-167	$2\text{PdF}_2 \rightarrow \text{PdF}_3 + \text{PdF}$	72
$\text{Pd} + 2\text{F}_2 \rightarrow \text{PdF}_4$	-769	$\text{PdF}_3 + 1/2\text{F}_2 \rightarrow \text{PdF}_4$	-142	$2\text{PdF}_3 \rightarrow \text{PdF}_6 + \text{Pd}$	335
$\text{Pd} + 5/2\text{F}_2 \rightarrow \text{PdF}_5$	-831	$\text{PdF}_4 + 1/2\text{F}_2 \rightarrow \text{PdF}_5$	-62	$2\text{PdF}_3 \rightarrow \text{PdF}_4 + \text{PdF}_2$	26
$\text{Pd} + 3\text{F}_2 \rightarrow \text{PdF}_6$	-920	$\text{PdF}_5 + 1/2\text{F}_2 \rightarrow \text{PdF}_6$	-89	$2\text{PdF}_4 \rightarrow \text{PdF}_6 + \text{PdF}_2$	159
				$2\text{PdF}_5 \rightarrow \text{PdF}_6 + \text{PdF}_4$	-27
				$\text{PdF}_5 + \text{Pd} \rightarrow \text{PdF}_3 + \text{PdF}_2$	-256
				$\text{PdF}_5 + \text{Pd} \rightarrow \text{PdF}_4 + \text{PdF}$	-158
				$3\text{PdF} \rightarrow \text{PdF}_3 + 2\text{Pd}$	33
				$5\text{PdF} \rightarrow 2\text{PdF}_2 + 3\text{Pd} + \text{F}$	181

^aADF, BP86, TZ2P, ZORA.

of the PdF_n ($n = 1-6$) species is thermodynamically favorable. We concentrated on the enthalpy terms on the assumption that the entropy contributions will be small due to the low temperature of experiment. In addition, calculating entropy and hence free energy relationships for matrix isolated species is nontrivial due to the quenching of the rotational and translational entropy components. The calculation of the F_2 bond enthalpy by DFT methods is notoriously challenging,⁷¹ but this only affects the absolute, rather than relative, values of the PdF_x thermochemical data.

Because of the F_2 dilution used in the matrix experiments it is expected that a range of species will be formed, and it is illustrative to use the stepwise thermochemistry to investigate the likelihood of formation of the species sequentially, and these are presented in Table 2 and graphically in Figure 4. These demonstrate that while all the $\text{PdF}_{n-1} + 1/2\text{F}_2 \rightarrow \text{PdF}_n$ reactions are thermodynamically favorable, they become

progressively less exothermic on going from PdF_2 to the higher coordination numbers. It should be noted that if fluorine atoms are present, the reactions will become much more favorable. The photolysis of F_2 in cryogenic matrices not only results in fluorine atoms but also these fluorine atoms are able to travel considerable distances beyond the immediate cage where they are formed.⁷²⁻⁷⁴ Table 2 and Figure 4 also highlight that PdF_5 is unstable with respect to disproportionation to PdF_6 and PdF_4 , and while the disproportionation of PdF_3 is predicted to be slightly endothermic (26 kJ mol^{-1}), it is still relatively favorable at the DFT level. While disproportionation of mononuclear complexes is not expected in dilute matrices, it gives some idea of the stability of the products formed. Therefore, the conclusion based on relativistic DFT-level thermochemistry is that the most stable species are PdF , PdF_2 , PdF_4 , and PdF_6 , followed by PdF_3 and then PdF_5 .

Electronic Absorption Spectroscopy. Initially, electronic absorption spectroscopy was used to confirm the presence of Pd atoms within the matrix using the thermal evaporation source. Historically, the assignment of the correct features to Pd atoms took time to resolve as it is very easy to form $\text{Pd}(\text{N}_2)$ and $\text{Pd}(\text{N}_2)_2$ even in the absence of a vacuum leak due to nitrogen adsorption onto the Pd filament.⁷⁵⁻⁸³ Note also that as Pd atoms have a $4d^{10}$ ground-state configuration, the propensity for dimer formation is small, and the intensity of any dimer bands is very weak.⁷⁷ Figure 5a confirms the presence of Pd atoms in 1% F_2/Ar matrices when thermal evaporation was used. Apart from the shoulder at 46 920 cm^{-1} , the spectral features at 40 310, 42 300, and 45 410 cm^{-1} are essentially identical to those of Pd atoms in argon matrices.⁷⁵⁻⁸² On annealing to 18 K the Pd atomic spectral features were replaced by broader ones at 40 210, 45 880, and 49 010 cm^{-1} . No further change was observed after broadband photolysis (Figure 5c). The very weak features in the 1% F_2/Ar spectra at ca. 30 000 cm^{-1} are most likely to be due to palladium dinitrogen species.^{79,81} When a 10% F_2/Ar matrix was used, a broad peak at 38 250 cm^{-1} was observed on deposition in addition to the broader Pd atomic spectral features at 40 200, 42 350, and 45 870 cm^{-1} (Figure 5d). The 38 250 cm^{-1} peak is not due to F_2 , as this is observed as the weak, broad feature at 35 200 cm^{-1} .⁵ On broadband photolysis (Figure 5e) no difference was observed, but on annealing to 18 K (Figure 5f), the atomic Pd features disappeared, to just leave the broad 38 250 cm^{-1} peak. In both sets of spectra there is also a weak and very broad band

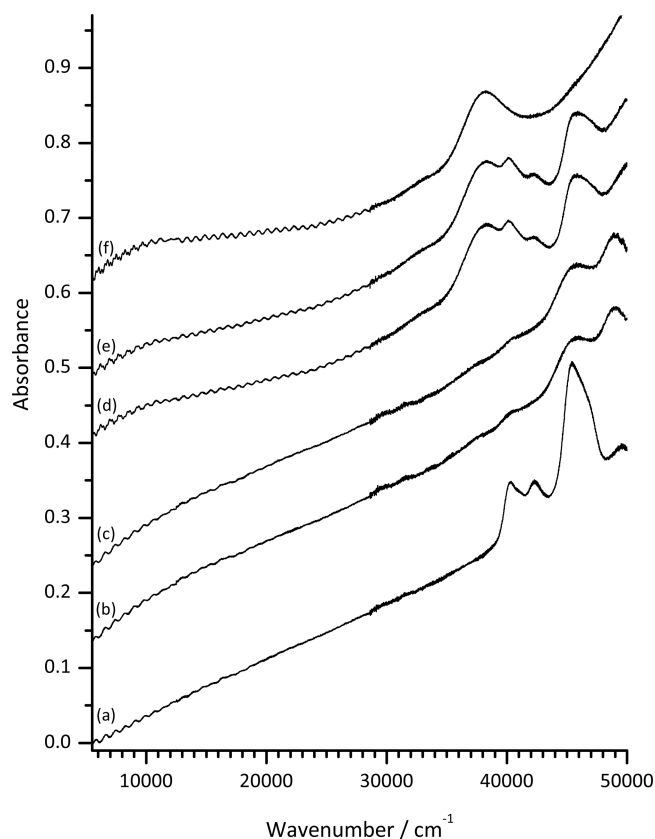


Figure 5. Electronic absorption spectra of Pd atoms and reaction products (a) in 1% F₂/Ar matrix after deposition, (b) after annealing to 18 K, (c) after broadband photolysis, (d) in 10% F₂/Ar matrix after deposition, (e) after broadband photolysis, (f) after annealing to 18 K.

at low energy that is only observed when the products bands are present. Therefore, these experiments confirm that atomic

Pd is being isolated in the thermal evaporation experiments and also indicate that there are at least two different species formed after annealing that are dependent of the F₂ concentration, with photolysis having little effect in this case either before or after annealing.

Infrared Spectroscopy. A large number of experiments were performed with a variety of matrix dilution ratios using fluorine-doped argon and neon matrices, as well as neat fluorine matrices. In addition, both thermal evaporation and laser-ablation techniques were used to generate palladium atoms, thus allowing for a comparison of the two methods. As in the case of the electronic absorption spectra, very weak bands arising from the ν_{NN} modes of Pd(N₂) and Pd(N₂)₂ complexes,^{84–86} as well as ν_{OO} modes of Pd(O₂),^{86,87} but not for (O₂)Pd(N₂)^{86,88} were observed in the IR spectra. These species arise from the reaction of palladium atoms with residual N₂ and O₂ in the matrix gases and the vacuum chambers and are a good indication that the experimental conditions were optimized for palladium atom matrix reactions.

Thermal Evaporation Experiments. When Pd atoms generated thermally from a Pd/Ta filament were condensed in a 2% F₂/Ar matrix a number of bands were observed in the $\nu_{\text{Pd-F}}$ region as shown in the survey spectrum (2 cm^{−1} resolution) in Figure 6a (Those at 667 and 662 cm^{−1} are due to gas-phase and matrix-isolated CO₂, respectively). On broadband photolysis (Figure 6b) the most marked differences are a reduction in intensity of the bands at 534 cm^{−1} (A) and 624 cm^{−1} (D) and an increase in the bands at 656 and 692 cm^{−1} (E), together with a slight change in the band at 617 cm^{−1} (C). On annealing to 20 K, there is a further increase in the band at 692 cm^{−1} (E). The intense peak at 540 cm^{−1} (B) remains invariant, while that at 617 cm^{−1} (C) remains largely unaffected by either photolysis or annealing.

At higher spectral resolution Pd isotope structure was observed on the bands labeled (A)–(E) in Figure 6, and this is shown in more detail in the higher-resolution (0.5 cm^{−1})

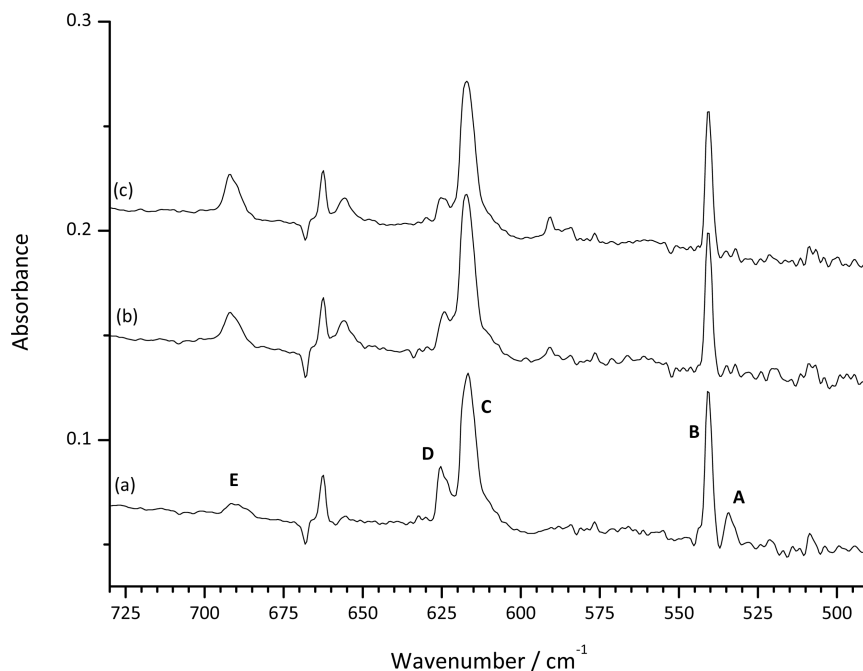


Figure 6. IR spectra (2 cm^{−1} resolution) of reaction products from thermally evaporated Pd atoms in a 2% F₂/Ar matrix (a) on deposition, (b) after broadband photolysis, (c) after annealing to 20 K.

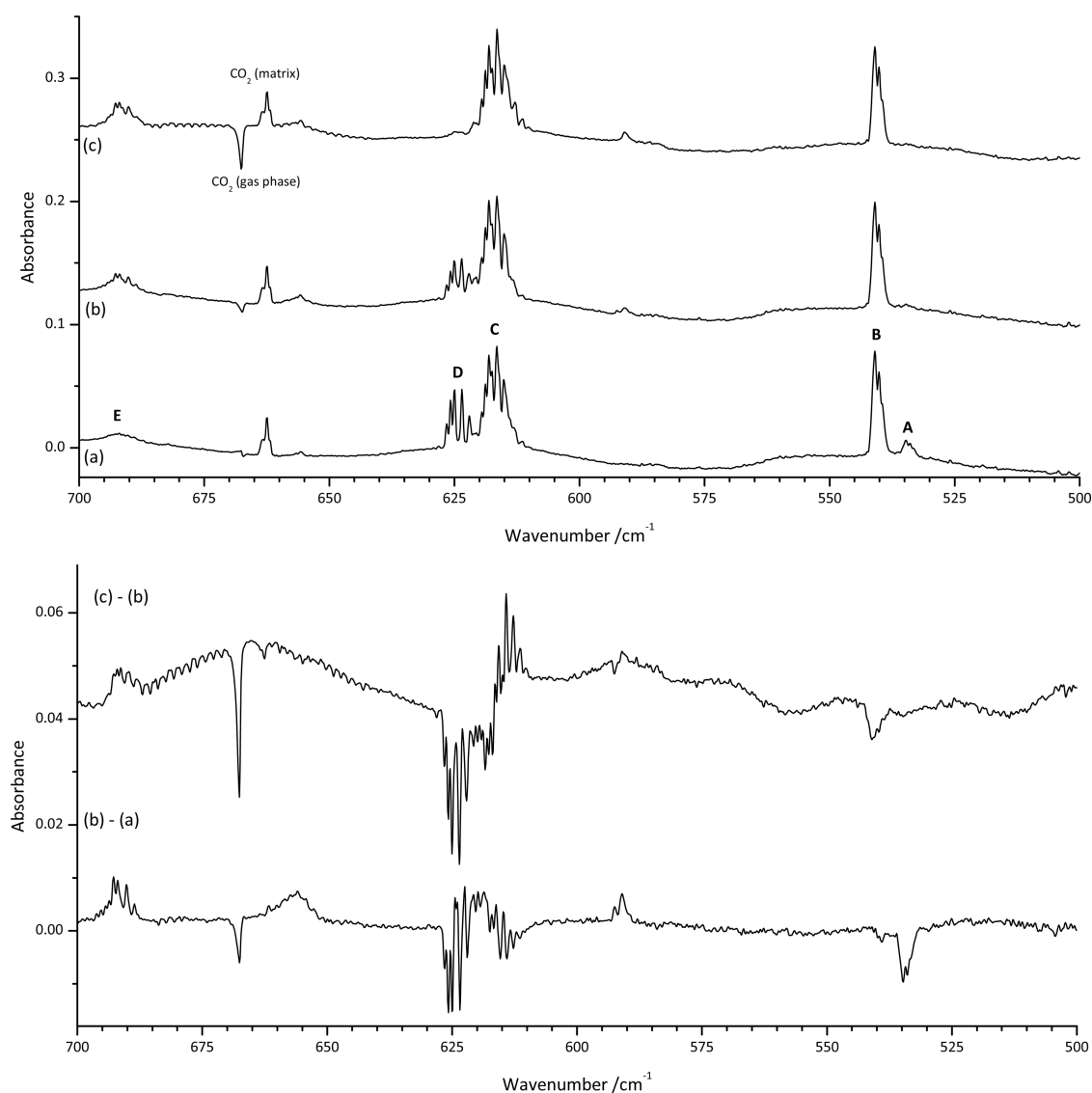


Figure 7. IR absorption (top) and difference (bottom) spectra (0.5 cm^{-1} resolution) of reaction products from thermally evaporated Pd atoms in a 0.5% F_2/Ar matrix (offset for clarity) (a) on deposition, (b) after Hg–Xe broadband photolysis, (c) after annealing to 25 K .

spectrum obtained when Pd atoms generated from a Pd/Ta filament were condensed in a 0.5% F_2/Ar matrix (Figure 7a). Peaks with Pd isotopic fine structure were observed centered at 624 cm^{-1} (D), 617 cm^{-1} (C), 540 cm^{-1} (B), and 534 cm^{-1} (A). There was also a weak broad feature potentially with Pd isotopic fine structure at 692 cm^{-1} (E). After Hg–Xe broadband photolysis (Figure 7b), the initially very weak peak at 692 cm^{-1} (E) grew in intensity, and this confirmed the presence of Pd isotopic structure on this band. Its relative intensity compared to the 617 cm^{-1} bands was less in the 0.5% F_2/Ar matrix than in the 2% F_2/Ar experiment. The effect of photolysis is shown more clearly in the difference spectra at the bottom of Figure 7. Although a new feature at 591 cm^{-1} also grew in on broadband photolysis in both the 0.5% and 2% F_2/Ar experiments, on careful analysis it was shown that this does not possess Pd isotopic structure, as it is made up of two bands that display different behavior on annealing and photolysis. A new peak at 656 cm^{-1} also appeared in both experiments, which while this displayed some structure, this was not consistent with a vibrational mode involving Pd. This peak was also observed in matrices with considerable CO_2 features,

together with a peak at 2356 cm^{-1} characteristic of HF-CO_2 ,⁸⁹ and with no other peaks displaying Pd isotope structure. Therefore, the peak at 656 cm^{-1} is assigned to the HF-CO_2 complex,⁸⁹ rather than a PdF_n complex. The peaks (D) centered at 624 cm^{-1} reduced in intensity slightly on photolysis; the structure on peak C at 617 cm^{-1} changed slightly, and the intensity of some weak peaks on the low energy side of the C peaks reduced. While there was no significant change in peak B at 540 cm^{-1} the feature at 534 cm^{-1} (A) all but disappeared on photolysis (The peak at 667 cm^{-1} is the Q-branch of the ν_2 mode of atmospheric CO_2 , and there is also evidence of the P and R branch structures. These are due to small variations in the atmospheric CO_2 levels between background and sample spectra, and become more marked at higher resolution). After the sample was annealed to 25 K (Figure 7c), the (E) peaks containing Pd isotope structure at 692 cm^{-1} grew, those labeled (B) at 540 cm^{-1} reduced in intensity slightly, while those at 534 cm^{-1} (A) completely disappeared. The (D) peaks at 624 cm^{-1} all but disappeared, and the structure within the C peaks at 617 cm^{-1} again changed slightly; weak peaks at slightly lower wavenumber than 617

cm^{-1} grew in intensity. While the peaks at both 624 cm^{-1} (D) and 534 cm^{-1} (A) reduced in intensity after broadband photolysis, this was not to the same extent, and the subsequent annealing behavior confirms that they do not belong to the same species. The peaks that show the most marked increase on photolysis are those labeled (E) at 692 cm^{-1} ; when annealed to 25 K these increase slightly again, accompanied by a more significant increase in those to the low-energy side of the peaks at 617 cm^{-1} (C). The behavior of the (E) peaks on photolysis and annealing is not correlated with any of the other peaks bearing Pd isotopic structure.

In a second experiment with a 0.5% F_2/Ar matrix, the peaks labeled (D) at 624 cm^{-1} were relatively more intense than the (C) peaks at 617 cm^{-1} , and no (A) peak was observed at 534 cm^{-1} . This behavior confirms that none of these bands are from the same species. On prolonged broad band photolysis in this second experiment, the 624 cm^{-1} (D) peaks were completely photobleached before annealing took place. The peaks at 692 cm^{-1} (E), 617 cm^{-1} (C), and 540 cm^{-1} (B) behaved in the same way on photolysis and annealing as in the first experiment, except that the 692 cm^{-1} (E) peak was not as intense. In this experiment, the weak peaks on the low-energy side of the C peaks grew on prolonged broadband photolysis but then reduced on annealing to 25 K, which is a reversal in behavior to the experiment above. The peak at 656 cm^{-1} again displayed no palladium isotope structure.

Therefore, from the survey spectra (Figures 6 and 7) it is clear that there are peaks centered at 692 cm^{-1} (E), 624 cm^{-1} (D), 617 cm^{-1} (C), 540 cm^{-1} (B), and 534 cm^{-1} (A), which all display Pd isotopic structure. In addition the photolysis and annealing behavior indicates that they each arise from distinct PdF_n species. The spectral features from the initial 0.5% F_2/Ar experiment shown in Figure 7 will be considered in detail in turn, starting with the lowest-energy ones.

Figure 8b shows in detail the bands at 540 cm^{-1} (B) and 534 cm^{-1} (A) (in Figure 7) after deposition of Pd atoms into a 0.5% F_2/Ar matrix. After broad-band photolysis (Figure 8c) there was a marked decrease in the intensity of the 534 cm^{-1} (A) peaks, and subsequent annealing to 25 K (Figure 8d) removed them altogether. It will be recalled from Figure 1 that the Pd isotope pattern associated with PdF is very different from that of PdF_2 . Although the Pd isotope structure on both of the features in Figure 8 is not fully resolved, the SVFF calculations (using values of 540.1 and 533.9 cm^{-1} for the ^{108}Pd components of the two bands, see Table 3) in Figure 8a confirm that both are consistent with a PdF unit rather than a PdF_2 unit.

In the thermal evaporation experiments there are three other sets of bands at 692 cm^{-1} (E), 624 cm^{-1} (D), and 617 cm^{-1} (C), all of which display characteristic Pd isotopic structure. The bands at $630\text{--}600\text{ cm}^{-1}$ immediately after deposition of palladium atoms in a 0.5% F_2/Ar matrix are shown in Figure 9f, and there is a difference in behavior between these two sets of bands on broadband photolysis and annealing. The intensity of the higher-energy set (D) centered at 624 cm^{-1} reduced slightly on broad-band photolysis (Figure 9g) and then disappeared on annealing to 25 K (Figure 9h). In other experiments with 0.5% F_2/Ar matrices the higher-energy multiplet at 624 cm^{-1} (D) had greater relative intensity than the (C) set at 617 cm^{-1} and could also be photobleached by prolonged photolysis. No other features in the ν_{PdF} region have the same photolysis and annealing behavior as these 624 cm^{-1} bands. The SVFF calculations in Figure 9a and Table 3 indicate that the Pd

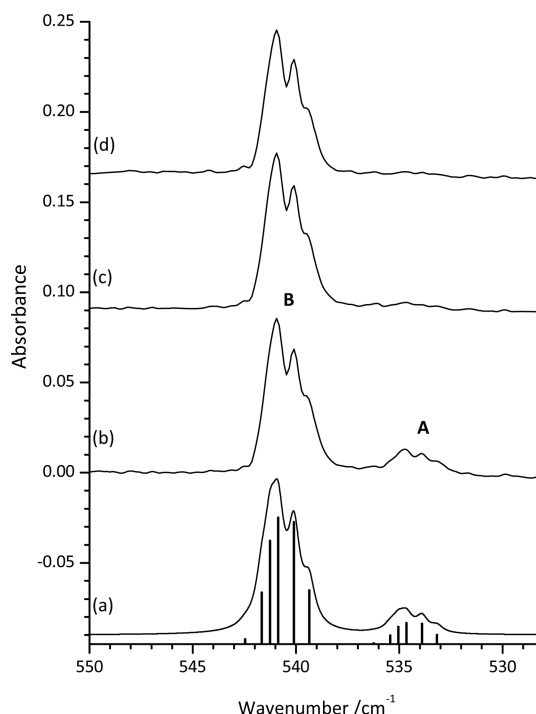


Figure 8. IR spectra of reaction products from thermally evaporated Pd atoms in a 0.5% F_2/Ar matrix (a) SVFF calculated spectrum for a PdF unit (^{108}Pd 540.1 cm^{-1} , ^{108}Pd 533.9 cm^{-1} , 0.7 cm^{-1} bandwidth), (b) on deposition, (c) after broad band photolysis, (d) after annealing to 25 K.

isotope pattern on the 624 cm^{-1} feature is consistent with a linear PdF_2 unit (the ^{108}Pd peak position of 623.5 cm^{-1} is used as the starting point for the calculations, because although it is not the most intense, it is clearly resolved). There is a slight reduction in the separation of the observed positions compared to the SVFF calculated values, which could be taken as an indication of slight bending of the PdF_2 , or an increase in the effective mass of the palladium atom, but the measurements are at the limit of the experimental uncertainty. Note that once deposition was complete, the 624 cm^{-1} features never grew in intensity, and they were only ever depleted by photolysis and annealing.

Within the set of (C) bands at 617 cm^{-1} , there is a slight change in the relative intensity of the components on both photolysis and annealing (Figure 9f–h), and this indicates that there are two Pd isotope patterns slightly offset from each other within this set of bands. The major component can be simulated with a linear PdF_2 unit with ^{108}Pd at 616.5 cm^{-1} as shown in Figure 9b and Table 3. The second set of bands consists of shoulders separated by $\sim 0.5\text{ cm}^{-1}$ from the main one. The peak at 617.5 cm^{-1} belonging to this set was used to simulate an SVFF linear PdF_2 isotope pattern using both ^{106}Pd and ^{108}Pd as the starting point. The former (Figure 9c) gave a very good fit when combined with the major component (Figure 9b) as shown in Figure 9d. The overall SVFF simulation using the three calculations involving linear PdF_2 units is shown in Figure 9e, and the match to the experimental data in Figure 9f is very good. To low energy of the main C peaks at 617 cm^{-1} there are a set of weak peaks at 614.2 , 612.7 , and 611.4 cm^{-1} indicative of Pd isotopic structure associated with a linear PdF_2 unit. These already weak features on deposition reduced on broadband photolysis but grew on

Table 3. Infrared Data for Palladium Atom F₂ Reaction Products in Cryogenic Matrices

thermal evaporation				laser ablation			
Hull (0.5% F ₂ /Ar)				Virginia 0.5% F ₂ /Ar	Freiburg Berlin 2% F ₂ /Ar	Freiburg Berlin 0.5% F ₂ /Ne	Berlin F ₂
A	observed	SVFF calculated ^a	assignment				
		536.2	¹⁰² PdF				
		535.4	¹⁰⁴ PdF				
		535.0	¹⁰⁵ PdF				
	534.7	534.7	¹⁰⁶ PdF				
	533.9	533.9 ^c	¹⁰⁸ PdF				
	533.2	533.2	¹¹⁰ PdF				
B	observed	SVFF calculated ^a	assignment				
		542.5	¹⁰² PdF				
		541.7	¹⁰⁴ PdF				
		541.3	¹⁰⁵ PdF				
	540.9	540.9	¹⁰⁶ PdF				
	540.1	540.1 ^c	¹⁰⁸ PdF				
	539.4	539.4	¹¹⁰ PdF				
C	observed	SVFF calculated ^b	assignment	observed	observed	observed	observed
		site A	site B				
		621.2					
			620.7				
	619.5	619.6	¹⁰⁴ PdF ₂	619.8			613.6
			619.1				
	618.8	618.8	¹⁰⁵ PdF ₂	618.9	618.8	651.5	612.9
			618.3				
	618.1	618.0	¹⁰⁶ PdF ₂	618.1	618.1	650.8	612.1
	617.5		617.5 ^c				
	616.5	616.5 ^c	¹⁰⁸ PdF ₂	616.6	616.5	649.2	610.6
D	616.0 (sh)		616.0				
	615.1	615.0	¹¹⁰ PdF ₂	615.1	615.1	647.7	609.1
	614.6 (sh)		614.5				
	observed	SVFF calculated ^b	assignment				
	628.1	628.3	¹⁰² PdF ₃ / ¹⁰² PdF ₆				
	626.5	626.6	¹⁰⁴ PdF ₃ / ¹⁰⁴ PdF ₆				
	625.7	625.8	¹⁰⁵ PdF ₃ / ¹⁰⁵ PdF ₆				
E	625.0	625.0	¹⁰⁶ PdF ₃ / ¹⁰⁶ PdF ₆				
	623.5	623.5 ^c	¹⁰⁸ PdF ₃ / ¹⁰⁸ PdF ₆				
	622.0	622.0	¹¹⁰ PdF ₃ / ¹¹⁰ PdF ₆				
	observed	SVFF calculated ^b	assignment				
	695.5	695.5	¹⁰² PdF ₄				
	693.6	693.6	¹⁰⁴ PdF ₄				
	692.7	692.8	¹⁰⁵ PdF ₄				
	691.9	691.9	¹⁰⁶ PdF ₄				
	690.2	690.2 ^c	¹⁰⁸ PdF ₄				
	688.5	688.6	¹¹⁰ PdF ₄				

^aAssuming a linear PdF unit. ^bAssuming a linear PdF₂ unit. ^cUsed to calculate other values.

annealing to 25 K (Figure 9h). However, in a second experiment they grew on prolonged photolysis and then reduced on annealing. Given how weak they are they were not included in the SVFF final fit.

The only remaining peaks displaying Pd isotope structure in Figures 6 and 7 are those labeled E at 692 cm⁻¹. These are barely present on deposition (Figure 10a) but grow on both photolysis (Figure 10b) and annealing to 25 K (Figure 10c). The SVFF simulation (Figure 10d and Table 3) is consistent with a species containing a linear PdF₂ unit. As for the 617 cm⁻¹ features (C) there is evidence for shoulders indicating two

species, but given the quality of the data they were not simulated in this case.

Therefore, the peaks labeled A and B are consistent with Pd–F units, while those labeled C, D, and E are consistent with linear F–Pd–F units. On the basis of both photolysis and annealing behavior, all the peaks with Pd isotopic structure appear to be from distinct species.

With the aim of increasing the proportion of the higher fluorides, 10% F₂/Ar matrices were also employed. However, broader bands were observed where it was impossible to identify any Pd isotopic structure. Given the number of bands that are expected in the $\nu_{\text{Pd-F}}$ region from F₂ impurity

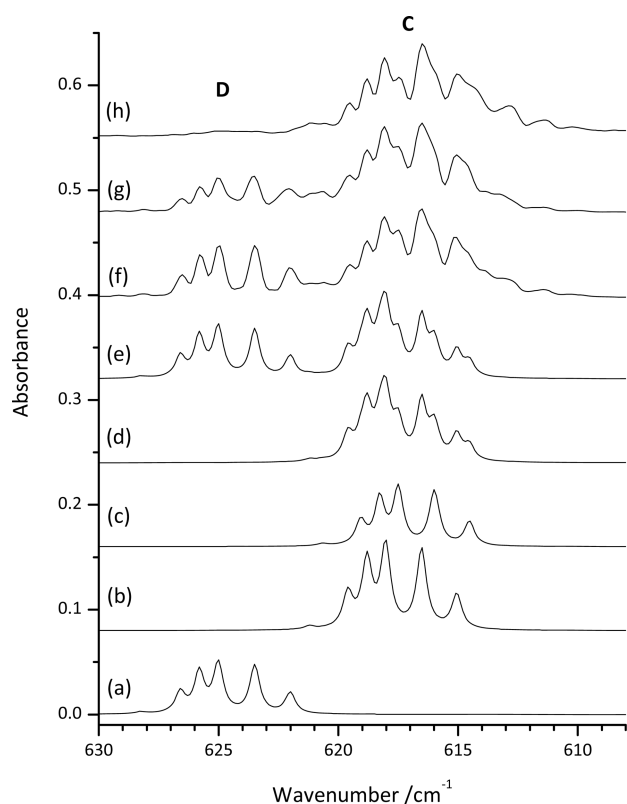


Figure 9. SVFF calculated spectra for a linear PdF_2 unit (a) ^{108}Pd 623.5 cm^{-1} , (b) ^{108}Pd 616.5 cm^{-1} , (c) ^{106}Pd 617.5 cm^{-1} , (d) sum of (b, c), (e) sum of (a, d). IR spectra of reaction products from thermally evaporated Pd atoms in a 0.5% F_2/Ar matrix (f) on deposition, (g) after broad band photolysis, (h) after annealing to 25 K .

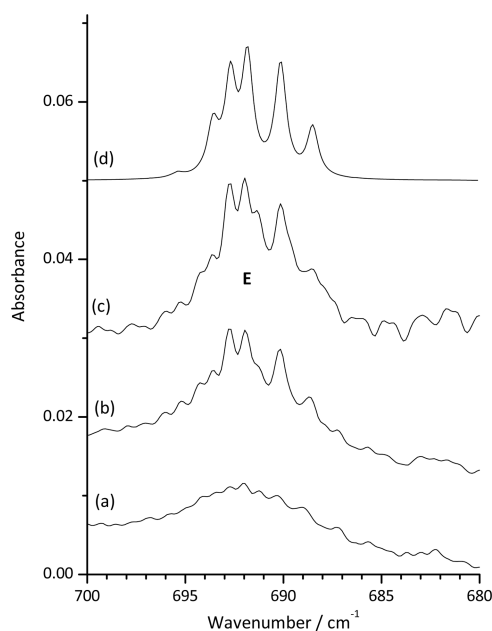


Figure 10. IR spectra of reaction products from thermally evaporated Pd atoms in a 0.5% F_2/Ar matrix (a) on deposition, (b) after broad band photolysis, (c) after annealing to 25 K , (d) SVFF calculated spectrum for a linear PdF_2 unit with ^{108}Pd at 690.2 cm^{-1} .

interactions this is especially problematic.⁵ A feature at 690 cm^{-1} was more intense than the overlapping, poorly resolved

features, at 615 and 607 cm^{-1} , and no bands were observed at 540 or 534 cm^{-1} , indicating that the higher wavenumber bands arise from higher oxidation state fluorides. On annealing to 25 K followed by broad-band photolysis the 690 cm^{-1} peak reduced in intensity, and a shoulder grew in at 681 cm^{-1} , which then grew on further annealing to 25 K . However, without Pd isotope patterns it is hard to assign these to PdF_n species with any certainty.

Laser Ablation Experiments. Figure 11 shows the IR spectra obtained in Virginia after laser-ablated Pd atoms were reacted with a 0.5% F_2/Ar matrix. In addition to the $[\text{F}_3]^-$ band at 510 cm^{-1} ,⁵³ a structured band with Pd isotopic structure (see insert) was observed at 617 cm^{-1} together with another band at 540 cm^{-1} , and these correspond to bands (C) and (B), respectively, in the thermal evaporation experiments. After annealing to 20 K , a very weak feature at 692 cm^{-1} was observed, which decreased on photolysis with $\lambda > 380\text{ nm}$ and full arc photolysis but then reappeared with increased intensity after annealing to 30 K . This corresponds to band (E) in the thermal evaporation experiments. In addition, annealing to 30 K resulted in the appearance of a new band (with Pd isotopic structure consistent with a linear PdF_2 unit) at 611 cm^{-1} . These peaks grew further after annealing to 35 K , while the intensity of the peaks at 692 , 617 , and 540 cm^{-1} all decreased. These new features are in a similar region to those observed in the thermal evaporation experiments to the low-energy side of the 617 cm^{-1} bands, but they are not at identical energy. Apart from the lack of the 624 cm^{-1} bands (which are very photosensitive), these observations are in very good agreement with the thermal evaporation data.

The results of the Pd laser-ablation experiments performed at Freiburg/Berlin with F_2 -doped argon matrices were also very similar to those observed from the thermal evaporation experiments and the Virginia based laser-ablation experiments, except that the $[\text{F}_3]^-$ band at 510 cm^{-1} ⁵³ was more intense relative to those of the PdF_n features. In a 2% F_2/Ar matrix (Figure 12), bands with Pd isotopic structure were observed on deposition at 617 cm^{-1} together with weaker features at 624 cm^{-1} , and these correspond to bands (C) and (D) in the thermal evaporation experiments. A weak feature, with poorly resolved Pd isotope structure, was also observed at 540 cm^{-1} in agreement with peak (B) in the thermal evaporation experiments. There is a weak peak at 657 cm^{-1} , but its assignment is complicated by the presence of atmospheric CO_2 at 667 cm^{-1} , and in the thermal evaporation experiments it was assigned to the HF-CO_2 complex.⁸⁹ When annealed to 25 K (Figure 12b) the bands centered at 617 cm^{-1} increased in intensity, with a subtle change in the structure, as also observed in the thermal evaporation experiments. On UV photolysis (Figure 12c), the 624 cm^{-1} bands disappeared, and while masked by the R branch structure of the bending mode of atmospheric CO_2 , a weak feature also grew in at 692 cm^{-1} , corresponding to peak (E) in the thermal evaporation experiments. In other argon experiments this feature was more marked.

Therefore, there is a high level of agreement between the argon matrix data for the products generated by thermal evaporation and both laser-ablation experiments.

When 0.5% F_2/Ne matrices were employed in Berlin (Figure 13), the only bands observed after deposition at 5 K to have Pd isotopic structure were at ca. 650 cm^{-1} , and these persisted after annealing to 8 K and then 10 K . As in the argon matrix case, an intense band at 524.8 cm^{-1} is assigned to $[\text{F}_3]^-$.^{52,53} In addition, a new band at 642 cm^{-1} bearing Pd isotopic structure

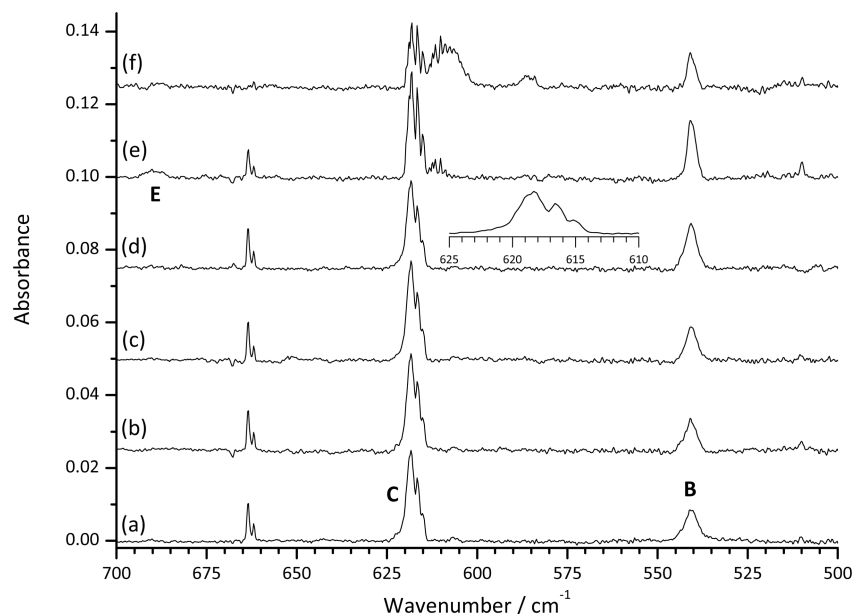


Figure 11. IR spectra of reaction products from laser-ablated Pd atoms in a 0.5% F₂/Ar matrix (a) on deposition, (b) after annealing to 20 K, (c) after photolysis >380 nm, (d) after full arc photolysis, (e) after annealing to 30 K, (f) after annealing to 35 K. (inset) Expansion of spectrum (d).

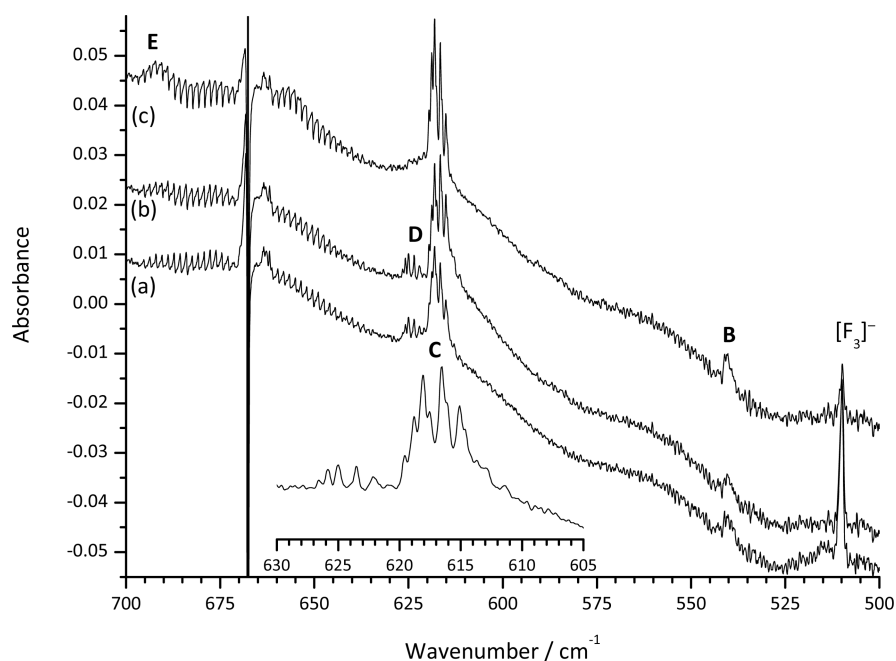


Figure 12. IR spectra of reaction products from laser-ablated Pd atoms in a 2% F₂/Ar matrix (a) on deposition, (b) after annealing to 25 K, (c) after 15 min UV irradiation. (inset) Expansion of spectrum (b).

appeared on annealing to 8 K. This correlates with the argon matrix laser-ablation experiments performed in Virginia, where bands with Pd isotopic structure to slightly lower energy of the main ones at 617 cm⁻¹ grew on high-temperature (35 K) annealing. The structured band in neon (Figure 13) at 650 cm⁻¹ exhibited strongest resolved Pd isotopic peaks at 651.0, 649.3, and 647.8 cm⁻¹, and these are all shifted by 32.8 cm⁻¹ from the most intense features in the corresponding 2% F₂/Ar spectrum (Figure 12, bands (C)), which showed strongest peaks at 618.2, 616.5, and 615.0 cm⁻¹. There were no features observed in these neon matrix data that corresponded to bands (A), (B), or (D). Although there was no clear evidence for the counterparts of the E bands at 692 cm⁻¹ in Ar, it should be

remembered that photolysis was usually necessary to observe them, especially at this level of F₂ dilution. However, in separate Ne matrix experiments a weak band was observed at 685 cm⁻¹ after annealing to 11.5 K, and after photolysis this increased in intensity at the expense of the 650 cm⁻¹ bands.

When neat F₂ was used as a matrix gas in the Berlin laser-ablation experiments (Figure 14), the only bands with clear Pd isotopic structure were observed at 614 cm⁻¹, which sharpened on annealing to 25 K, decreased on 365 nm photolysis, and then decreased again on annealing to 30 K. The band at 586 cm⁻¹ is due to OOF.⁹⁰ In addition, there is a band at 690 cm⁻¹, which although masked by the atmospheric CO₂ features does correspond to the set of bands labeled (E) in the argon matrix

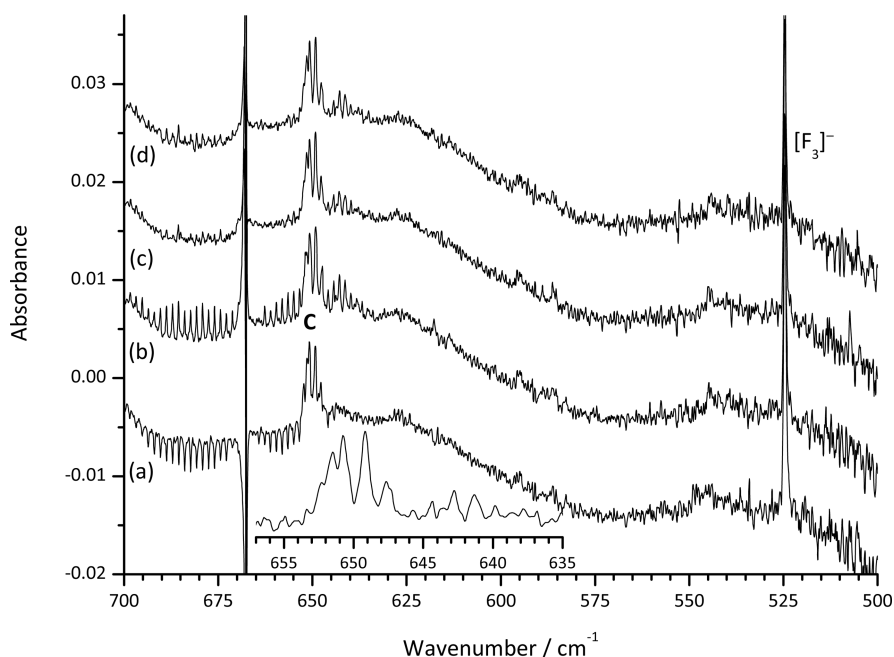


Figure 13. IR spectra of reaction products from laser-ablated Pd atoms in a 0.5% F₂/Ne matrix (a) on deposition, (b) after annealing to 8 K, (c) after annealing to 8 K for 1 min, (d) after annealing to 10K. (inset) Expansion of spectrum (d).

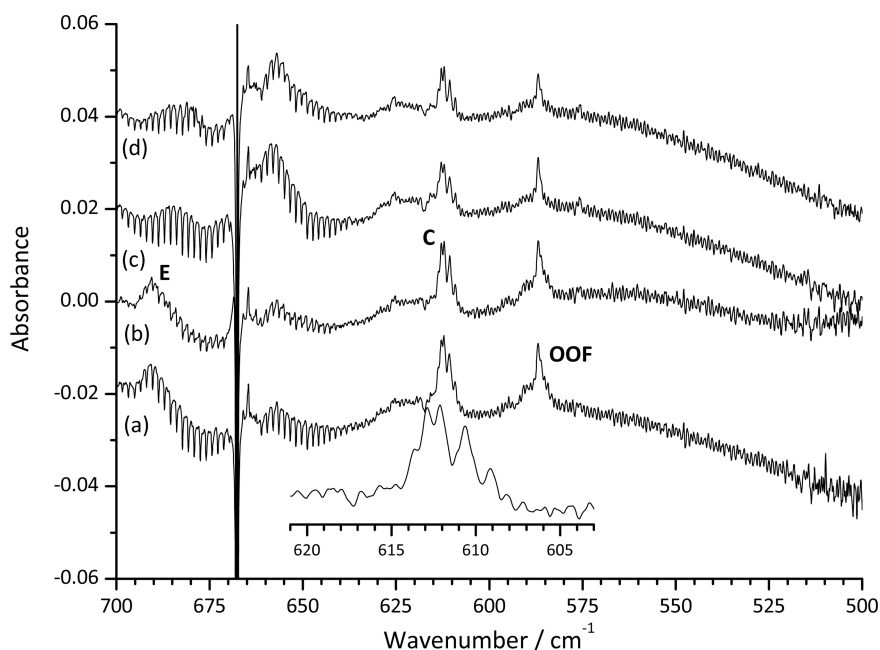


Figure 14. IR spectra of reaction products from laser-ablated Pd atoms in a neat F₂ matrix (a) on deposition, (b) after annealing to 25 K, (c) after photolysis at 365 nm, (d) after annealing to 30 K. (inset) Expansion of spectrum (b).

thermal evaporation experiments. There is no evidence for either of the sets of peaks labeled **A** or **B** confirming that these belong to lower oxidation state species. Published work on neat halogen matrices is fairly limited, but it has been noted that the matrix shifts for argon and neat fluorine matrices are very similar.⁹¹ A shift of 10 cm⁻¹ was observed for AuCl₃ between a 5% Cl₂/Ar matrix and a neat Cl₂ matrix.⁴⁹ Therefore, the 614 cm⁻¹ bands in neat F₂ most likely to correspond to those at either 617 cm⁻¹ (**C**) or 624 cm⁻¹ (**D**) were observed in the argon matrices. As the (**C**) bands were observed in all experiments it is most plausible to assign those in the neat F₂

experiments to the same carrier as **C** in the argon matrix experiments.

DISCUSSION

The electronic absorption spectra indicate that under thermal evaporation conditions Pd atoms are being isolated in the argon matrices, which go on and react with the fluorine, and that while in these experiments photolysis had little effect, there are at least two new species formed on annealing that are dependent on the F₂ concentration. The observed transition energies (38 000–49 000 cm⁻¹) are significantly greater than

those calculated by David et al. using TDDFT for transitions to the lowest-energy excited state in PdF_6 (15 560, 22 760 cm^{-1}),¹¹ although there is a very broad and weak feature at lower energy observed only when the product bands are present.

Although it has been possible to identify the vibrational modes involving palladium, the lack of fluorine isotopic data makes unambiguous assignment of the vibrational modes to specific palladium fluorides very challenging. What is clear is that overall there is very good agreement between the three argon matrix experiments (thermal evaporation in Hull and laser ablation in Virginia and Freiburg/Berlin) and also between the different matrix gases (F_2/Ar , F_2/Ne , F_2). In summary, the features at 692 cm^{-1} (E), 617 cm^{-1} (C), and 540 cm^{-1} (B) in the IR spectra of F_2 -doped Ar matrices containing Pd atoms were common to all thermal evaporation and laser-ablation experiments. There are no counterparts of the 534 cm^{-1} (A) band in either laser-ablation experiment, and the 624 cm^{-1} (D) features observed from thermal evaporation are observed in some of the Freiburg/Berlin laser-ablation experiments but not the Virginia ones. Neon was used as a matrix gas in the laser-ablation experiments at Freiburg/Berlin, and in these experiments only one band at 650 cm^{-1} with clear Pd isotopic structure was observed on deposition, although a feature at 685 cm^{-1} was detectable among the atmospheric CO_2 features, together with a weak set of peaks to low wavenumber of the 650 cm^{-1} feature that appeared at relatively high annealing temperatures. The neat F_2 experiments were only performed at Berlin, and as with the Freiburg/Berlin neon matrix experiments, only yielded one set of bands with clear Pd isotopic structure, but there was evidence for a peak at 690 cm^{-1} among the atmospheric CO_2 peaks. The absence of the bands labeled D in some of the laser-ablation experiments is most likely due to the effects of the intense radiation field associated with ablation, as these bands were very sensitive to both photolysis and annealing, and were never observed to increase in intensity once deposition was complete. Therefore, the absence of some bands may be as a result of photobleaching of photosensitive species.

The changes in the relative intensity of the IR bands in the different F_2/Ar matrices imply that in general those at lower wavenumber are associated with lower coordination number/oxidation state palladium fluorides than those at higher wavenumber. The annealing and photolysis behavior of the absorption bands in the thermal evaporation experiments of Pd atoms indicate that none of the IR bands with Pd isotope structure at 692 cm^{-1} (E), 624 cm^{-1} (D), 617 cm^{-1} (C), 540 cm^{-1} (B), and 534 cm^{-1} (A) are from the same species. As there is no evidence for second bands with the same annealing and photolysis behavior as any of these five, it is not easy to assign any of them to either PdF_3 or PdF_5 , but the expected weaker bands could be of too low intensity to be observed above the noise level, or hidden under another more intense feature. The palladium fluorides are predicted (at the relativistic DFT level) to have intense bands at 534 cm^{-1} (PdF), 634 cm^{-1} (PdF_2), 648.0 cm^{-1} (PdF_5 and PdF_6), 662 cm^{-1} (PdF_3), and 664 cm^{-1} (PdF_4) with weaker features at 565 cm^{-1} for PdF_3 and 633 cm^{-1} for PdF_5 , respectively. It should be remembered that PdF_2 ³⁶ and PdF_4 ^{41,42} are well-characterized solid-state materials, but PdF_3 is mixed-valent and is best thought of as $\text{Pd(II)[Pd(IV)F}_6]$, with both palladium atoms in an octahedral fluoride environment.^{37–40}

The 540 cm^{-1} peak (B) was common to both the laser-ablation and thermal evaporation experiments using argon matrices, while the 534 cm^{-1} peak (A) was only observed in the thermal evaporation work and was readily removed by photolysis and annealing. The Pd isotope patterns on the 540 and 534 cm^{-1} peaks (Figure 8) are consistent with the assignment of these two peaks to PdF (or PdF units). The almost complete reduction in the intensity of the 534 cm^{-1} band after broad-band photolysis and its disappearance on annealing is not associated with a decrease in any of the other features, including the bands at 624 cm^{-1} ; therefore, it cannot be assigned to a PdF unit in PdF_3 or PdF_5 . The calculated value for PdF is 531⁴⁵ or 533.9 cm^{-1} from this work. Therefore, these bands can be readily assigned to PdF . The most straightforward assignments are for the 540 cm^{-1} bands to PdF and the 534 cm^{-1} bands to PdF in a slightly different site, which can be removed by photolysis and annealing. A possibility is that PdF is isolated in close proximity to an F atom or F_2 molecule with which it can readily react resulting in an increase in the peaks at 692 cm^{-1} and possibly 617 cm^{-1} . The observation of PdF on deposition of thermal Pd atoms with F_2 indicates that the $\text{Pd} + \text{F}_2 \rightarrow \text{PdF} + \text{F}$ reaction is spontaneous and that F atoms are therefore present in the matrix, in addition to F_2 . Similar evidence was also observed in the analogous Ti work.⁵⁰ In dilute F_2/Ne matrices a corresponding weak band with poorly resolved palladium isotope structure was observed at 545 cm^{-1} . In neat F_2 matrices there was no evidence for a peak belonging to PdF , as to be expected. This work represents the first spectroscopic characterization of molecular PdF .

In the 630–600 cm^{-1} region of the argon matrix data there are four IR bands displaying Pd isotopic structure in the thermal evaporation data, one set at 624 cm^{-1} , a second overlapping pair at 617 cm^{-1} , and a very weak set at 612 cm^{-1} . The 617 cm^{-1} bands are also in both of the laser-ablation experiments, but the 624 cm^{-1} bands are only present in the Freiburg/Berlin laser-ablation work and not in the Virginia experiments. However, high-temperature annealing in the Virginia experiments resulted in bands at 611 cm^{-1} .

The 617 cm^{-1} features were observed in all of the thermal and laser-ablation experiments with argon matrices, and with Pd isotopic structure consistent with a linear PdF_2 unit it seems reasonable to assign them to PdF_2 , especially as the calculations indicate this has the lowest vibrational frequency apart from PdF . The second set of bands displaying Pd isotope structure overlapping these could be due to another species, but as the separation between them is of the order of 0.5 cm^{-1} a more reasonable assignment would be to a second site for PdF_2 . While the two sets could feasibly arise from the two modes expected for either D_{2d} or D_{2h} distorted PdF_4 , the second site explanation is much more likely, especially as a similar situation was observed for linear TiF_2 in argon matrices, where two sites could also be modeled successfully.⁵⁰ As the 617 cm^{-1} bands assigned to PdF_2 were present in all dilute F_2/Ar matrices, it would seem sensible to assign the only bands observed with clear Pd isotopic structure in 0.5% F_2/Ne matrices at 650 cm^{-1} to PdF_2 as well. This is a relatively large argon-to-neon matrix shift, which may be compared with the 15 cm^{-1} shift observed for the matrix isolated $[\text{F}_3]^-$ anion,⁵³ and 22 cm^{-1} for FeF_2 , 15.1 cm^{-1} for FeF_3 , and 21.6 cm^{-1} for FeF_4 .⁵² The large matrix shift of 32.8 cm^{-1} indicates that the Pd center is vulnerable to interactions with the matrix atoms because it is not saturated with bound F atoms. In neat F_2 matrices bands with Pd isotopic structure were observed at 614 cm^{-1} , and as PdF_2 was observed

in all the other experiments, it is reasonable to assign these features to PdF_2 as well. These data represent the first spectroscopic characterization of molecular PdF_2 .

There were weak peaks to lower wavenumber than the (C) peaks in both the thermal evaporation and laser-ablation experiments after photolysis and annealing but not at identical values or with identical behavior. The 611 cm^{-1} peaks observed after relatively high-temperature annealing in the Virginia laser-ablation experiments clearly have Pd isotopic structure consistent with a linear PdF_2 unit (Figure 11), whereas this is less clear in the thermal evaporation data. These are most likely due to unidentified aggregation products formed on high-temperature annealing.

The peaks at 692 cm^{-1} in dilute F_2/Ar matrices are very weak after deposition but grow on photolysis and annealing in both the thermal evaporation and laser-ablation experiments, indicating that they are the result of species formed from reaction of Pd or PdF_n with either fluorine atoms or fluorine molecules. They are also relatively more intense in the matrices with a higher concentration of F_2 . The Pd isotopic structure from the thermal evaporation experiments (Figure 10) is consistent with a linear PdF_2 unit, and there does not appear to be any other $\nu_{\text{Pd-F}}$ bands that have the same photolysis and annealing behavior. In neat F_2 matrices corresponding features were observed at 690 cm^{-1} , and in dilute Ne matrices they were found at 685 cm^{-1} . The relativistic DFT calculations indicate that PdF_4 will have the highest energy $\nu_{\text{Pd-F}}$ modes of the palladium fluorides, and our CC calculations on PdF_4 and PdF_6 (see Supporting Information) also indicate that the IR-active $\nu_{\text{Pd-F}}$ modes of PdF_4 will be higher than those of PdF_6 . Therefore, on the basis that solid-state PdF_4 is well-known;^{41,42} the concentration, annealing, and photolysis behavior of the peaks at 692 cm^{-1} in argon matrices (and 690 cm^{-1} in F_2 and 685 cm^{-1} in F_2/Ne) indicate that they can be assigned to PdF_4 . From the experimental data it is not possible to tell whether this is strictly square planar (D_{4h}) or slightly distorted (D_{2d} or D_{2h}), but the possibility of shoulders might indicate a small distortion, although a site effect explanation would be just as reasonable. As for PdF and PdF_2 , this represents the first characterization of molecular PdF_4 .

This leaves the assignment of the peaks at 624 cm^{-1} in dilute argon matrices. The Pd isotope pattern (Figure 9) indicates the presence of linear (or nearly linear) PdF_2 units. The annealing and photolysis behavior indicates that they belong to a reactive/unstable species with the major beneficiary appearing to be the bands at 692 and 612 cm^{-1} . Under no conditions were these bands seen to grow once deposition had finished, and their reduction on annealing implies thermal instability, suggesting either a gain or loss of F to form a more stable species. With the lack of fluorine isotopic data it is a real challenge to be able to assign these with certainty to PdF_6 , PdF_5 , or PdF_3 .

The relativistic DFT calculations predict the IR-active $\nu_{\text{Pd-F}}$ mode of PdF_6 to be 18 cm^{-1} higher than in PdF_2 and 15 cm^{-1} lower than PdF_4 , both of which would be reasonably consistent with an assignment of the 624 cm^{-1} peaks to PdF_6 . Neat F_2 experiments would be expected to stabilize the highest palladium fluoride, but the only band with clear Pd isotopic structure observed was at 614 cm^{-1} , which is best assigned to PdF_2 in comparison with all the other data. There was also evidence for another peak in neat F_2 matrices at 690 cm^{-1} , which was assigned to PdF_4 . If the peaks at 624 cm^{-1} in argon matrices are assigned to PdF_6 it is very hard to explain why these PdF_6 features at 624 cm^{-1} should be present in the matrix

before PdF_4 at 692 cm^{-1} , and that the latter is only really formed after photolysis and annealing, as well as there being no evidence for the 624 cm^{-1} bands in the neat F_2 matrix (unless those at 614 cm^{-1} assigned to PdF_2 are instead due to PdF_6). The IR-active mode of PtF_6 is at 705 cm^{-1} ,^{32,33} and for the nearest 4d/5d pair to Pd/Pt, the IR-active modes are at 724 cm^{-1} (RhF_6)⁹² and 719 cm^{-1} (IrF_6).³³ On this basis, as well as a band at 711 cm^{-1} being assigned previously to PdF_6 ,^{27,28} an alternative assignment is that the peaks at 692 cm^{-1} could be due to PdF_6 , and those at 624 cm^{-1} could be due to PdF_4 . However, this is not supported by both the DFT and CC calculations, which indicate that PdF_4 will have higher IR-active $\nu_{\text{Pd-F}}$ modes than PdF_6 , and the expectation that PdF_4 would be more stable than PdF_6 . Therefore, there is little convincing evidence for PdF_6 in any of these experiments, but it is not completely ruled out.

Another possibility is that with the 692 cm^{-1} bands being assigned to PdF_4 , the photolysis and annealing behavior of those at 624 cm^{-1} indicate that these could be assigned to PdF_3 , and that the second, weaker (calculated relative intensity of 3:1), IR-active mode is either too weak to be observed above the noise level or is masked by other features in the spectrum. The SVFF calculations indicate that the PdF_2 unit might be slightly bent or the effective mass of the palladium is slightly increased, both of which would be consistent with T-shaped PdF_3 . However, the relativistic DFT calculations indicate that the most intense $\nu_{\text{Pd-F}}$ IR-active mode in PdF_3 will overlap that of PdF_4 ca. 30 cm^{-1} higher than that for PdF_2 , but experimentally these bands are much closer to the those of PdF_2 rather than PdF_4 . While it is tempting to assign the 534 cm^{-1} feature as the second IR-active mode of PdF_3 , all the evidence points to the 624 and 534 cm^{-1} peaks being from different species. The photolysis and annealing behavior of the bands at 612 cm^{-1} are also different than that of the 624 cm^{-1} set, so these are not the second set of PdF_3 (or PdF_5) bands either. Therefore, while the assignment of the 624 cm^{-1} peaks to PdF_3 is indicated by the experimental observation of their formation on deposition and subsequent depletion by annealing and photolysis, it is not completely satisfactory, as there is only one band observed in the IR spectrum, and its relative position with respect to the other PdF_n species is not that predicted by the calculations.

The calculated values for the IR-active $\nu_{\text{Pd-F}}$ modes in PdF_5 are at 648 and 633 cm^{-1} , with an intensity ratio of ca. 10:1, and while these are more compatible with the peaks at 624 cm^{-1} , the calculations indicate that PdF_5 is the least stable of the palladium fluorides and is unstable with respect to disproportionation to PdF_4 and PdF_6 . While PtF_5 is known,^{93,94} there do not appear to be any reputable reports for PdF_5 .¹ It is hard to rationalize why PdF_5 should be formed but not PdF_3 or even PdF_6 . Therefore, it seems that assigning the 624 cm^{-1} features to PdF_5 is the least likely option.

Therefore, it is not possible to make an unambiguous assignment of the 624 cm^{-1} peaks in argon matrices, with PdF_6 , PdF_3 , and PdF_5 all being possibilities, but PdF_6 and PdF_3 are the most plausible. While the calculations (in terms of the position of the vibrational frequencies) indicate that PdF_6 is the most probable, the experimental observations of the 624 cm^{-1} bands being more intense on deposition than those assigned to PdF_4 at 692 cm^{-1} , and also very susceptible to photolysis and annealing, would indicate that assigning them to PdF_3 is the more sensible option. What is clear is that the species giving

rise to the 624 cm⁻¹ bands is very photosensitive and thermally unstable even at cryogenic temperatures.

CONCLUSIONS

This work has shown that there is a high degree of consistency between the thermal evaporation and laser-ablation experiments but that the high photon flux associated with the latter may photobleach some products. There are a total of seven sets of IR-active bands that display Pd isotope behavior in the $\nu_{\text{Pd-F}}$ region when Pd atoms (produced by thermal evaporation or laser ablation) are trapped in F₂-doped Ar matrices. In analogous neon and neat F₂ experiments only one band displayed clear Pd isotopic structure, but there was evidence for others when taken together with the argon data. This work has been able to assign absorptions at 540 and 617 cm⁻¹ in argon matrices with confidence to PdF and PdF₂, respectively. The peaks at 534 cm⁻¹ are also consistent with a Pd–F unit but do not correlate with any other peaks, and they are assigned to PdF in a different site. Likewise, there is also a site effect on the PdF₂ bands at 617 cm⁻¹. This leaves the sets of peaks at 692, 624, and 612 cm⁻¹, which contain linear PdF₂ units, and do not seem to have any other sets of bands associated with them. Those at 692 cm⁻¹ have behavior consistent with a higher fluoride than PdF₂, and as the calculations suggest that PdF₄ will have the highest $\nu_{\text{Pd-F}}$ mode these have been assigned to PdF₄. This is supported by the relative stability of PdF₄. The Pd isotopic structure on the bands at 624 cm⁻¹ indicates the presence of linear or nearly linear PdF₂ units, and the photolysis and annealing indicates that there are no other IR-active modes above the noise level associated with them and that they are photosensitive and thermally unstable on annealing, with the biggest beneficiaries appearing to be the bands at 692 and 612 cm⁻¹. This suggests that there is either a gain or loss of F to form a more stable species. From the data available the most plausible assignment is to either PdF₆ or PdF₃, with the latter being the most reasonable based on the experimental evidence, but this is by no means unambiguous. Therefore, while there is no convincing evidence for PdF₆, this detailed study has provided experimental evidence for PdF, PdF₂, and PdF₄ for the first time. The lack of PdF₆ is perhaps not that surprising as it is known that XeF₂ will oxidize PtF₄ and PdF₃ but will not oxidize PdF₄.³⁹

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b02273.

A table of nonrelativistic DFT and CCSD computational results from this work, together with literature values for PdF_n species. (PDF)

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Notes

The authors declare no competing financial interest.

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